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APPLICATION OF THE CRITICAL VOLTAGE EFFECT TO THE STUDY
OF ORDERING IN ALLOYS

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ABSTRACT

Calculated values have been obtained for the critical voltage (V_c) of several ordered alloys as a function of degree of long-range order (S). Most systems have a reflection showing a critical voltage within the range of our microscope (220-650kV) but the variation with S is generally predicted to be very small. Experiments on Cu_3Au and Ni_4Mo further indicate that the critical voltage effect is not useful for obtaining new information about the early stages of ordering transformations.

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1. INTRODUCTION

In electron microscopy, it has been well established that under certain systematic or simultaneous diffraction conditions a high order reflection can show a minimum of intensity. This minimum occurs at a voltage dependent on the structure factor of the reflections that are operating (Nagata and Fukuhara, 1967; Uyeda, 1968; Watanabe, Uyeda and Kogiso, 1968; Metherell and Fisher, 1969; Lally, Humphreys, Metherell and Fisher, 1972). The significance of this phenomenon, which has become known as the critical voltage effect, for metallurgical applications is that since the structure factor of a reflection depends on the composition of the alloy and, for the case of an ordered alloy, on the degree of order, the voltage at which the minimum occurs depends on these variables. Usually systematic diffracting conditions are obtained and the second order reflection is utilized for measuring critical voltages. Examples of the use of this technique for studying local variations of composition have been previously described (Lally et al, 1972; Butler, 1973, 1974). The purpose of the present paper is to evaluate whether or not the critical voltage effect can provide useful new data on ordering reactions in alloys, especially on the local degree of order in transformed regions.

The critical voltage may be determined to an accuracy of about $\pm 0.5\%$ by the Kikuchi line method (L.E. Thomas, 1972; Bell and Thomas, 1972) and to about $\pm 1-2\%$ by the bend contour method (Lally, et al, 1972; Butler, 1972). The first calculations of the variation of critical voltage (V_c) with degree of order (S) for Cu_3Au indicated a change of about 50% for V_c of the (400) reflection between the fully ordered and disordered states (Lally, et al, 1972).

Initially, the technique appeared to be most promising. However, more recent experimental work (L.E. Thomas, Shirley, Lally and Fisher, 1974), which has been substantiated in the present study, has shown that the variation is much smaller than was originally expected.

In this paper, the variation of critical voltage with degree of long-range order has been calculated for a range of ordering alloys, in the voltage range presently available at Berkeley (200-650kV). Experimental investigations into the Cu_3Au and Ni_4Mo systems were also performed in order to assess the practical implications of these calculations.

2. THEORY

The theoretical calculations of the critical voltage are essentially identical to those of Metherell and Fisher (1969) and Lally et al., (1972). The eigenvectors and eigenvalues of the solutions of many-beam Bloch wave equations were calculated for the propagation of electrons in a periodic potential (Hirsch, Howie, Nicholson, Pashley and Whelan, 1965). The critical voltage occurs when, at an exact reflecting condition, two of the eigenvalues are the same and the two corresponding eigenvectors exchange symmetry. In practice, this yields an intensity minimum for the appropriate reflection, provided the specimen is sufficiently thick.

Initially, all likely systematic rows of reflections were scanned in the voltage range of interest and a critical voltage detected by this exchange of symmetry. Further refinement to $\pm 5\text{kV}$ was then performed using the same criterion. The scattering factors used were those of Doyle and Turner (1968) and, since the trend of results was of major interest, corrections using the Debye-Waller factor and accurate

lattice parameters were not included. The degree of order was taken into account by calculating the scattering factor of the required reflection from the known structure of the alloy with the Bragg-Williams probability of the atoms being on specific sites. The absolute values of V_c are therefore not accurate but the degree of change of V_c upon ordering is reasonably well indicated.

The results of these calculations are shown in Fig. 1, with the reflection indices, for convenience, referring to the fundamental disordered lattice. They may be summarised as follows:

(i) The variation of V_c with degree of order, S , is not marked in many systems, the most promising alloys being those with large differences in atomic scattering factors between the species of the alloy. For example, Cu_3Au is indicated to have the largest change ($\sim 200\text{kV}$ for the (400) reflection), whereas for the isostructural transformation $\text{f.c.c.} \rightarrow \text{Ll}_2$, Co_3V^* shows little or no change at all. Similarly, larger variations are generally present in the Au_4Cr system compared to isostructural Ni_4Mo , with the exception of the $\frac{7}{5}$ (420) reflection.

(ii) A change of V_c with S only occurs for reflections in systematic rows containing superlattice reflections. Thus, for Ni_4Mo , which has no $\{h00\}$ superlattice reflections, the (400) critical voltage should show no change on ordering. This has possible practical applications since it has been suggested that Ni_4Mo may order by way of a spinodal-type fluctuation with local changes in molybdenum concentration (Okamoto and Thomas, 1971). These changes may be detected due to the change of V_c with composition rather than degree of order in this particular case.

* This is the initial ordering reaction in Co_3V .

(iii) Many of the reflections showing a critical voltage effect in the voltage range considered are superlattice reflections. Since their intensity is considerably smaller than those for fundamental reflections the experimental determination of V_c would be less precise and hence the accuracy of such measurements reduced.

Conventional transmission electron microscopy has been very successful in elucidating later stages of ordering reactions (e.g. Tanner and Leamy, 1974), but it is the initial stages of ordering and short range order about which improved data are required. Thus, utilisation of the V_c effect when there are only small variations, or application of superlattice critical voltage effects which are extremely difficult to detect due to the low intensity and diffuseness of superlattice reflections in the early stages of ordering, do not appear to be viable for obtaining new information about many ordering reactions. Therefore, these calculations indicate that only in very few circumstances would the critical voltage effect be useful in studying the early stages of ordering.

3. EXPERIMENTAL PROCEDURE

Specimens of Cu 25.1% Au and Ni 19.7% Mo were prepared for electron microscopy by jet polishing 3mm diameter discs. The electropolishing conditions used for Cu₃Au were 360 mls acetic acid, 15 mls distilled water and 75 gms Cr₂O₃ at 70 volts and for Ni₄Mo 2:1 H₂SO₄:H₂O at 5 volts. Critical voltage determinations were carried out in an Hitachi HU 650 high voltage electron microscope with a continuously variable accelerating voltage. The nominal voltage settings were checked periodically using the Kikuchi map method described by Thomas, (1970).

Both Kikuchi line and bend contour methods were utilized for the V_c determination whenever possible. The former, illustrated in Fig. 2, involves orientation of a flat area of the specimen to the exact Bragg position of the disappearing reflection, without simultaneously exciting other non-systematic reflections, and observing the voltage at which a minimum occurs in this Kikuchi line intensity. Diffraction patterns taken with a fully focused second condenser lens (Butler, 1972,1973) were found to be most convenient for this method, with the photographic plates processed in a weak developing solution (~10% of normal strength). An accuracy of ± 5 -10kV was attained at 500kV, including experimental errors in the voltage determination.

The bend contour method is shown in Fig. 3, in which the disappearance of the bend contour in the appropriate dark field micrograph was observed. The specimen was oriented so that narrow bend contours were obtained approximately perpendicular to the edge of the specimen. Thus, the main specimen requirement of this method is a highly bent area of the foil, in contrast to the flat area necessary for the Kikuchi lines. Identical areas could not therefore be examined by both methods, but the agreement between them for the same specimen was found to be good. The bend contour disappears over a range of voltages but, using a detailed series of micrographs, an accuracy of ± 10 -20kV at 500kV was achieved. Finally, rather long exposure times (approximately two minutes) were necessary to record these images on conventional electron image plates as a low electron current density is required to minimise beam heating of the specimen. In order to avoid image drift high resolution micrographs were taken using x-ray film plates for which exposures of several seconds were sufficient.

4. EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Cu_3Au

The variation of critical voltage with degree of order (determined from x-ray intensity measurements) for Cu_3Au is shown in Fig. 4. It can be seen that the change of V_c between fully disordered and ordered states is only 60kV, much smaller than predicted by the calculations. The rate of change of V_c with S is also very slight initially (e.g. an increase of only 10kV up to $S = 0.7$). This indicates that the detection of the initial stages of ordering in Cu_3Au by the determination of an average critical voltage is considerably less precise than by conventional x-ray diffraction methods. However, it does offer in principle the possibility of observing highly ordered domains ($S \sim 1$) existing in a less ordered matrix ($S = 0 - 0.5$) by imaging the specimen at the matrix critical voltage so enhancing contrast (Bell and Thomas, 1972). Since the critical voltage of the ordered regions is substantially higher, they should stand out as bright regions in the (400) bend contour. By raising the imaging voltage and observing the disappearance of such regions, their critical voltage and hence local degree of order should be able to be determined. However, in practice, experiments of this type for partially ordered and short-range ordered Cu_3Au were not successful. This was thought to be due both to the poor resolution limit of our 650kV microscope ($\sim 20\text{\AA}$) and to the relatively small difference in V_c between ordered and disordered material. Another problem is the rather insensitive variation of bend contour intensity with voltage as the following explanation shows.

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Although the appropriate bend contour disappears at V_c , there is also an appreciable voltage range over which the contour cannot be detected or is very weak (e.g. Fig. 3). Micrographs taken on either side of this range allow the determination of V_c fairly precisely (± 10 kV), but the contour itself may not be present over a range of ~ 50 – 60 kV. Thus, when the matrix contour has disappeared at V_c , the brightness of the ordered domain is still weak, since the difference of critical voltage is relatively small, and the resultant contrast will be low. This is further enhanced by the small size of ordered domains in the initial stages of ordering (Sinclair and Thomas, 1975). The behaviour of bend contour disappearance is known to be reliable for specimen thicknesses greater than five or six extinction distances (100 kV) and it is such areas which are examined in V_c determinations. The ordered domains which form during the early stages of ordering in Cu_3Au are only $\sim 25\text{\AA}$ in diameter (Sinclair and Thomas, 1975). Thus, if the intensity of a bend contour is low, even 30 kV away from V_c , the absolute electron intensity from a small region only ~ 1 – 2% of this thickness, and producing only a weak bend contour effect, would be further reduced. Therefore, the resultant domain visibility would be correspondingly poor.

A study of the variation of V_c for the superlattice (500) reflection was also attempted but this proved to be unsuccessful. In the fully and partially ordered states the (500) Kikuchi line was too broad for precise V_c determination even in areas where the (400) Kikuchi line was very sharp. Dark field micrographs revealed little change in bend contour intensity throughout the available voltage range. It may be

appreciated that in the early stages of ordering the superlattice intensity is extremely low and a continuous superlattice bend contour is not obtained since ordered domains exist discretely in the matrix. Thus, utilisation of the (500) critical voltage, which is predicted by the calculations to show only minor changes upon ordering also does not appear to be experimentally viable for studying ordering in Cu_3Au .

Finally it may be noted that the absolute values of V_c found in the present study are in good agreement with those reported recently by Thomas et al., (1974) . Thus, in the fully ordered stage identical results are obtained ($420 \pm 10\text{kV}$ compared with $425 \pm 3\text{kV}$ found by Thomas et al., 1974), but the present values for disordered and partially ordered Cu_3Au are slightly lower ($360 \pm 10\text{kV}$ compared to $381 \pm 3\text{kV}$ from the data of Thomas et al., 1974). These data are currently being analysed (Rocher, 1974, private communication) to correct the atomic scattering factors of Cu and Au at lower values of $\frac{\sin \theta}{\lambda}$ than is possible from measurements on the pure f.c.c. metals (since the lowest $\frac{\sin \theta}{\lambda}$ value occurs for {111} in f.c.c. metals but for {100} in the L1_2 structure). The discrepancy between the experimental results and those of the simple dynamical calculations (as in the present paper) was first attributed to a necessary correction in the Debye temperature of the ordered alloy (Thomas et al., 1974). However, these more recent calculations still yielded results 10% higher than the experimental values. Use of the refined atomic scattering factors together with the corrections of Thomas et al., (1974) bring the calculated critical voltages to within experimental error of those observed (Rocher, 1974, private communication).

4.2 Ni_4Mo

A small increase in the (400) critical voltage was found on ordering Ni_4Mo , from $460 \pm 10\text{kV}$ in the disordered state to $490 \pm 5\text{kV}$ in the ordered state. Since no superlattice reflections are present in the {h00} systematic row, this change must be due to an effective change in Debye temperature of the alloy, which was not taken into account in the preliminary calculations. As for Cu_3Au , this difference is insufficient for utilisation in our study of ordering.

Short range order in this alloy is characterised by the presence of diffuse scattering at $(1\frac{1}{2}0)$ positions in the diffraction pattern. One possible explanation for this is the existence of microdomains with an imperfectly ordered DO_{22} structure (Okamoto and Thomas, 1971), which is based on the alloy composition Ni_3Mo . Local composition changes may occur to accompany this type of ordering and these also would give rise to local variations in critical voltage. The variation of V_c with composition (estimated using the value of 610kV for 0% Mo) is 7.5kV per at % Mo, approximately twice as large as the variation expected from three-beam calculations, as found by Butler (1973) for other nickel based alloys containing heavier elements. The difference in V_c between regions with 20 and 25% Mo is only 40kV . Experimentally no microdomains were observed in the bend contour of Ni_4Mo at the matrix critical voltage (e.g. Fig. 5). This failure to image the domains is thought to be due to the small difference in V_c as explained by the arguments presented for the similar situation existing in Cu_3Au .

The determination of the $\frac{7}{5}$ (420) and $\frac{11}{5}$ (420) critical voltages in ordered Ni_4Mo was also attempted by the Kikuchi line method, as the superlattice Kikuchi lines were found to be very sharp. However, the intensity of these respective lines was too low to be detected in the diffraction pattern throughout the whole range 200-650kV, even on over-exposed photographic plates. The specimen was tilted into nearby orientations (e.g. $\underline{g} = \frac{6}{5}$ (420) in order to establish that sharp Kikuchi lines were indeed present in the area from which the diffraction pattern was being taken (e.g. Fig. 6). Consequently the critical voltage for these reflections could not be established.

4.3 Mg_3Cd

The critical voltage for the $\frac{3}{2}$ (11 $\bar{2}$ 0) and $\frac{7}{2}$ (10 $\bar{1}$ 0) reflections of ordered Mg_3Cd could not be found within the range of our microscope (J. Dutkiewicz, 1974, private communication). This may have resulted from the influence of the fine domain structure (Dutkiewicz and Thomas, 1975) on the dynamical behaviour of electrons travelling through the crystal rather than due to incorrect predictions of the calculations shown in Fig. 1. The fundamental (10 $\bar{1}$ 1) critical voltage was also below the minimum obtainable voltage of 220kV (J. Dutkiewicz, 1974, private communication).

5. CONCLUSIONS

1. Both the theoretical and experimental results indicate that, in the alloy systems examined, only small changes occur in the critical voltage upon ordering. Thus critical voltage measurements do not seem to be useful application of transmission electron microscopy for studying the early stages of ordering reactions in alloys.

2. Examination of disappearing bend contours for domains with a different degree of order than the surrounding material, which are easily distinguishable in conventional dark field micrographs taken using superlattice reflections, did not resolve the domains in Cu_3Au nor Ni_4Mo .

3. The average critical voltage may be determined by the Kikuchi line method utilising electron diffraction patterns or, in a more localised area, using the bend contour method. Neither appears to be more beneficial for yielding information about the average degree of order than conventional x-ray techniques.

4. The bend contour method, although providing information on a localised scale, is not sufficiently sensitive for studying ordering reactions especially at the level necessary for yielding new data about the initial stages of the transformation. This may be compared with the success of the lattice imaging technique employed at conventional voltages for similar studies (Sinclair, Schneider and Thomas, 1975).

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FIGURE CAPTIONS

Fig. 1. The theoretical variation of critical voltage with degree of order for a variety of alloy systems. The indices of the reflections showing a critical voltage effect are indicated, based on the fundamental disordered lattice.

- (a) Cu_3Au and Co_3V : fcc $\rightarrow$ Ll_2
- (b) Fe_3Al : bcc $\rightarrow$ DO_3
- (c) Au_4Cr : fcc $\rightarrow$ Dla
- (d) Ni_4Mo : fcc $\rightarrow$ Dla
- (e) CuPt : fcc $\rightarrow$ Ll_1
- (f) Mg_3Cd : hcp $\rightarrow$ DO_{19}

Fig. 2. Kikuchi line method of determining V_c for the (400) reflection of fully ordered Ni_4Mo . The Kikuchi line passing through the (400) diffraction spot shows an intensity minimum at V_c (490kV).

Fig. 3. Bend contour method of determining V_c for the (400) reflection of disordered Ni_4Mo . The low visibility of the bend contour can be seen to occur over a range of voltages near V_c (460kV).

Fig. 4. Variation of critical voltage (V_c) of the (400) reflection of Cu_3Au with Bragg-Williams degree of long-range order (S).

Fig. 5. Centered (400) dark field micrograph of disordered Ni_4Mo at and below the critical voltage. Ordered domains, with a different critical voltage from the matrix, cannot be detected.

Fig. 6. Kikuchi line intensities in fully ordered Ni_4Mo at 500kV.

a) $\underline{g} = \frac{6}{5}(420)$, b) $\underline{g} = \frac{7}{5}(420)$, c) $\underline{g} = \frac{8}{5}(420)$. The $\frac{7}{5}(420)$ line is extremely weak, being undetectable throughout our available voltage range. Thus the corresponding critical voltage cannot be determined.

-15-

XBL 754-6143A

Fig. 1.

485 kv

490 kv

495 kv

XBB 754-3246

↑
(000)

↑
(400)

Fig. 2.

-17-

535 kv

485 kv

460 kv

435 kv

XBB 754-3247

Fig. 3.

XBL 754-6144

Fig. 4.

-19-

435 kv

460 kv

XBB 754-3254

Fig. 5.

$\frac{6}{5}(420)$

$\frac{7}{5}(420)$

$\frac{8}{5}(420)$

↑ (000) ↑ (420) XBB 754-3244 ↑ (840)

Fig. 6.

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